Synthesis and characterization of highly pure azido-functionalized polyhedral oligomeric silsesquioxanes (POSS)[†]

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Novel azido-functionalized POSS were synthesized, which could serve as nanoprecursors for higher-order molecular construction of organic-inorganic hybrids *via* "click" chemistry.

Since Huisgen reported that the 1,3-dipolar cycloaddition reaction between azide and terminal or internal alkynes can smoothly form a stable 1,2,3-triazole linkage in high yield and purity, many reports have widely used this reaction for constructing diverse molecular structures.¹

Meanwhile, much attention has been given to polyhedral oligomeric silsesquioxanes (POSS), especially to octahedral octasilsesquioxanes (T_8), having an octacyclic inorganic silicon and oxygen framework covered externally by various organic substituents.² The octasilsesquioxanes have shown a great potential for many applications such as electronics,³ optics,⁴ surface-modified supports,⁵ catalyst,⁶ and OLEDs.⁷

To further widen aspects of the application of POSS chemistry it is very important to utilize new types of reactions. Complete functionalization with novel reactive groups, thus providing the opportunity to design and build materials with well-defined dimensions possessing nanophase behaviour is a case in point. Introduction of substituents to T_8 has been mostly achieved by hydrosilation,⁸ Heck,⁹ and cross-metathesis¹⁰ reactions. We have been working on the azide function to combine organic substituents and the POSS core, but only a few reports have attempted to introduce the azide function to POSS derivatives.¹¹ Further, some important aspects of the reaction were not well-established.

We herein report on the clean and quantitative introduction of azide groups from a newly synthesized hepta(isobutyl)substituted- T_8 (2) and double-decker silsesquioxane (5) to provide 3 and 6 as mono- and diazido-functionalized POSS, respectively. Moreover, the independent report of cage rearrangement of the T_8 structure (7) under azidation reaction toward the multi azido-functionalized T_8 (8), T_{10} (9) and T_{12} (10) POSS is presented for the first time.

The novel precursors **2** and **5** were prepared following the reaction of known hepta(isobutyl)- T_7 -trisilanol (1)^{2f} with 3-chloropropyltrichlorosilane and double-decker octasilsesquioxane-tetraol tetrasodium salt (4)^{2m} with (3-chloropropyl)- methyldichlorosilane (Scheme 1). The azidation at room temperature to 45 °C proceeded very slowly and it was difficult to obtain a complete conversion. Moderately high temperature (about 70 °C) and less than three times excess of NaN₃ in DMF–THF mixed solvent (7 : 2) were key to achieve a high yield of **3** by clean reaction. Conversion of **2** was accelerated in the presence of THF probably because of improved solubility of the starting material. When the temperature was raised above 80 °C, materials was observed to decompose, and to change into higher molecular weight compounds.

Almost quantitative azidation of 2 to 3 (93% yield) could be achieved within 24 h, as confirmed by ¹H NMR by the shift from 3.53, 1.82 and 0.75 (3-chloropropyl) to 3.27, 1.74 and 0.69 (3-azidopropyl) ppm. Conversion of 5 to 6 was similarly carried out to give almost quantitative yield. These reactions smoothly proceeded without any cage rearrangement.

Novel precursor **5** exists as a mixture of *cis* and *trans* isomers, as indicated by ²⁹Si NMR at -18.35, -78.51, -79.46 ppm (*trans*), and -18.35, -78.51, -79.40, -79.49 ppm (*cis*) isomers. So far this mixture was unable to be seperated by column chromatography. Accordingly, azidation of **5** gave an isomeric mixture of **6**. Careful recrystallization of **6** using THF-methanol (1 : 1) gave pure crystalline *trans*-isomer, the structure of which was confirmed by single-crystal X-ray structural analysis (Fig. 1).‡

Meanwhile, we noticed extensive rearrangement of the T_8 cage under azidation condition of octakis(3-chloropropyl)silsesquioxane $(7)^{12}$ to produce a thermodynamically stable mixture of octakis(3-azidopropyl)silsesquioxane (8), deca(3-azidopropyl)silsesquioxane (9), and dodeca(3-azidopropyl)silsesquioxane (10) (Scheme 2), probably because of the necessary use of pure DMF of higher polarity as the solvent under severer reaction condition and longer reaction time to achieve a complete conversion of eight functional groups.

This phenomenon strongly suggested that the Si–O–Si bonds in the T_8 silsesquioxane cores were cleaved by strongly nucleophilic N_3^- , resulting in cage opening and silsesquioxane fragmentation. Reassembly of the T_8 cage and other size-cage silsesquioxanes has been found to occur under certain reaction conditions.²ⁿ Herein, we first report that sodium azide may play a dual role as a supplier of azide groups and as a nucleophile to induce cage rearrangement. Less steric hindrance, compared with other substituent groups (isobutyl or phenyl), on the silsesquioxane core of highly reactive 3-chloropropyl groups led to cage cleavage and rearrangement in the presence of sodium azide.

Careful separation using 1 g of sample by use of column chromatography (run through twice), led not only to ${\bf 8}$ but

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Scheme 1 Introduction of mono- and diazide functions to T_8 and double-decker silsesquioxane cages. (a) Conversion of 2 to 3 in DMF–THF (7 : 2), 0.025 mol L⁻¹ for functional group with 3 eq. NaN₃ at 70 °C for 24 h; (b) conversion of 5 to 6 in DMF–THF (5 : 2), 0.020 mol L⁻¹ with 3 eq. NaN₃ at 60 °C for 24 h.



Fig. 1 X-Ray crystallographic structure of trans-6.

also 9 and 10 being isolated in pure form. The first separation using ethyl acetate–hexane (2 : 5) as eluent could isolate only 8 ($R_f = 0.60, 0.25$ g, the actual yield of 8 is probably a little higher) in pure form; 9 and 10 gave very close R_f values (0.55),

and could not be separated. A second separation using ethyl acetate-hexane (2 : 9) gave 9 ($R_{\rm f} = 0.35, 0.45$ g), and 10 $(R_{\rm f} = 0.30, 0.18 \text{ g})$ as pure compounds. ²⁹Si NMR of the cage 8 (T₈) and 9 (T₁₀) showed singlets at -67.04 and -68.94 ppm, respectively. The signal of 9 (T₁₀) consisting of eight- and tenmembered rings resulted in an upfield shift about -1.90 ppm from that of 8. The ²⁹Si chemical shifts of 10 (T_{12}) appeared at -68.69 and -71.36 ppm with an integral ratio of 1 : 2 corresponding the presence of two different types of silicon atom in the cage of D_{2d} symmetry. Four 10-membered rings were obviously connected and rolled up to each other by sharing two disiloxane linkages (in total eight silicon atoms), leaving one silicon atom in each ring unconnected (four Si atoms). Upon connection of a pair of silicon atoms via a siloxane linkage, two eight-membered rings would be formed (so in total four eight-membered rings).¹³ Such cage rearrangement was reported by Rikowski and Marsmann.¹⁴ Ge et al. apparently reported the azidation reaction of 7 under more rigorous conditions, which might lead to various products.11c

In conclusion, novel mono- and diazido-functionalized POSS precursors (3 and 6) were successfully synthesized, as well as a cage rearrangement for the less sterically hindered T_8 cage (7) to T_8 (8), T_{10} (9), and T_{12} (10) cages. Functionalization of POSS in the presence of sodium azide is thus demonstrated.



Scheme 2 Cage rearrangement of T_8 cage 7 upon full introduction of azide functions leading to 8, 9 and 10; DMF, 0.077 mol L⁻¹, 1.5 eq. NaN₃, at 60 °C for 16 h.

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Notes and references

‡ *Crystal data*: C₅₆H₅₈N₆O₁₄Si₁₀, M = 1319.96, triclinic, space group $P\bar{1}$, a = 9.923(2), b = 13.285(3), c = 13.987(7) Å, U = 1557.98(9) Å³, T = 93 K, Z = 1, 17 649 reflections measured, 5487 unique ($R_{int} = 0.042$) which were used in all calculations. R_w (all data) = 0.1652.

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